

POLYMERS COMPRISING IN THEIR SKELETON AN ENDO ETHYLENIC
UNSATURATION, AND PREPARATION PROCESSES THEREFOR

DESCRIPTION

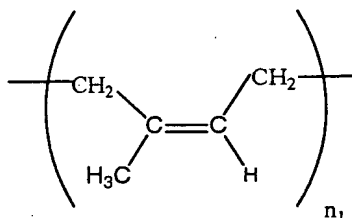
5 TECHNICAL FIELD

The present invention relates to novel polymers comprising in their skeleton an endo ethylenic unsaturation, and also to a process for manufacturing such polymers.

10 PRIOR ART

Polymers containing an Endo ethylenic unsaturation, which are generally synthesized from monomers containing two conjugated double bonds in their skeleton, are often referred to by the general
15 term "diene polymers".

Among the diene polymers that are the most common, mention may be made of rubber, also known as polyisoprene, this polymer consisting of a cis repeating unit having the following formula:



20

n_1 corresponding to the number of repeating units present in the said polymer.

It is harvested from rubber tree sap or may be obtained synthetically from isoprene via a Ziegler-
25 Natta polymerization.

A diene polymer of structure similar to that of rubber is polybutadiene, obtained from butadiene also by Ziegler-Natta polymerization.

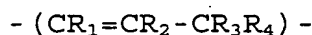
Butadiene also forms part of the constitution of the copolymer poly(styrene-butadiene-styrene), which is more commonly known by the abbreviation SBS or the trivial name hard rubber. This copolymer is a block copolymer successively comprising a long polystyrene chain, a long polybutadiene chain and again a long polystyrene chain. This copolymer especially forms part of the constitution of shoe soles and tyres.

Without being exhaustive, another diene polymer that may also be mentioned is polychloroprene, more commonly known under the name Neoprene. This polymer is obtained synthetically by polymerization of chloroprene, of formula $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$.

DESCRIPTION OF THE INVENTION

The aim of the present invention is to propose novel polymers comprising in their skeleton an Endo ethylenic unsaturation, and also processes for preparing these polymers that are simple to perform.

Thus, one subject of the invention is novel polymers whose skeleton comprises a sequence of units, the said units being identical or different and corresponding to formula (I) below:



(I)

in which:

- R_1 represents a hydrogen atom or a hydrocarbon-based group chosen from linear or branched alkyl groups containing from 1 to 20 carbon atoms, cycloalkyl groups containing from 3 to 8 carbon atoms, alkoxy groups containing from 1 to 20 carbon atoms, aryl groups containing from 6 to 20 carbon atoms and aryloxy groups containing from 6 to 20 carbon atoms;
 - R_2 represents a halogen atom or a hydrocarbon-based group chosen from linear or branched alkyl groups containing from 1 to 20 carbon atoms, cycloalkyl groups containing from 3 to 8 carbon atoms, alkoxy groups containing from 1 to 20 carbon atoms, aryl groups containing from 6 to 20 carbon atoms and aryloxy groups containing from 6 to 20 carbon atoms;
 - the radicals R_3 and R_4 , which may be identical or different, correspond to the same definition as R_1 , on condition that at least one of the radicals R_3 and R_4 represents, within each unit, a hydrogen atom;
- the said radicals R_1 , R_2 , R_3 and R_4 possibly comprising, when they represent a hydrocarbon-based group, one or more substituents chosen from halogen groups, alkyl groups of 1 to 20 carbon atoms, alkoxy groups of 1 to 20 carbon atoms, aryl groups of 6 to 20 carbon atoms, aryloxy groups of 6 to 20 carbon atoms and amino groups.

It is pointed out that, according to the invention, the term "amino group" means a primary, secondary (or monosubstituted) or tertiary (or disubstituted) amine group. The possible substituents may be alkyl groups.

The polymers according to the invention comprise in each unit of formula (I) an endo ethylenic unsaturation, this endo ethylenic unsaturation being located between two consecutive units of formula (I),
5 all three being carbon atoms.

Thus, by virtue of this arrangement, these polymers may have higher rigidity than that of their diene analogues (i.e. those having a sequence of units with an ethylenic unsaturation every four carbon atoms
10 between two adjacent units).

These polymers may correspond to any type of polymer comprising a sequence of units of formula (I). It is pointed out that the term "sequence" means the conjunction of at least two consecutive units of
15 formula (I), preferably at least 4 and even more preferably at least 10.

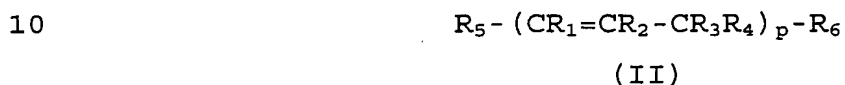
More specifically, these polymers may correspond to polymers whose skeleton consists solely (with the exception of the end units) of units of
20 formula (I), these units possibly being identical or different. It is noted that the units of formula (I) may be different, which is the case when R_1 , R_2 , R_3 and R_4 are different from one unit to the other. These polymers may also correspond to polymers whose skeleton
25 consists partly of units of formula (I) and of other units, for example units derived from the units of formula (I), such as diol units.

According to the invention, the sequence of units of formula (I) may comprise at least one group
30 chosen from the group consisting of $C=O$, $C=NOH$ or $CHOH$, and linear or branched alkylenediyl groups containing

from 4 to 20 carbon atoms, and mixtures thereof. In other words, in the sequence of units (I), the groups as defined above may interconnect between two units (I) of the sequence.

5 Preferably, the polymers of the invention have a molar mass of from 500 g/mol to 2 000 000 g/mol.

Particular polymers that fall within the general definition of the present invention correspond to formula (II) below:



in which the radicals R_1 , R_2 , R_3 and R_4 are as defined above, R_5 represents a linear or branched alkyl group containing from 1 to 20 carbon atoms, a cycloalkyl
15 group containing from 3 to 20 carbon atoms or an aryl group containing from 6 to 20 carbon atoms, R_6 represents an-OH, primary amine, thiol -SH, halogen or -CHO group, a group derived from -CHO, an ester group, an optionally substituted amide group or an azide group
20 -N₃, and p is an integer ranging from 4 to 10 000.

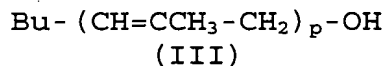
According to the invention, the term "optionally substituted amide" means, in the text hereinabove and hereinbelow, a primary (or unsubstituted) amide, a secondary (or monosubstituted)
25 amide or a tertiary (or disubstituted) amide. The possible substituents may be alkyl groups.

The term "-CHO derivative" means, in the text hereinabove and hereinbelow, a group resulting from a nucleophilic addition of a nucleophilic reagent
30 to -CHO, such as an imine, oxime or hydrazine group.

In formula (II), R_1 , R_3 and R_4 are as defined for the unit of formula (I) and may be identical. As an example of a radical R_1 , R_3 and R_4 that may be used, mention may be made, for example, of
 5 hydrogen.

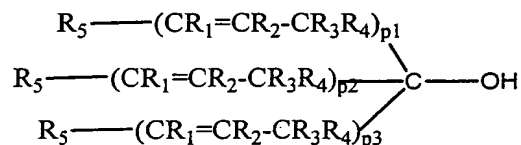
In formula (II), R_2 may be a linear alkyl group containing from 1 to 20 carbon atoms, such as a methyl group, and R_5 may be a linear alkyl group containing from 1 to 4 carbon atoms, such as a butyl
 10 group.

When R_1 , R_3 and R_4 represent H, R_2 represents $-\text{CH}_3$, and R_5 represents a butyl group $\text{CH}_3-(\text{CH}_2)_3-$ (referred to as Bu in the formula below) and R_6 represents $-\text{OH}$, the polymer corresponds to formula
 15 (III) below:



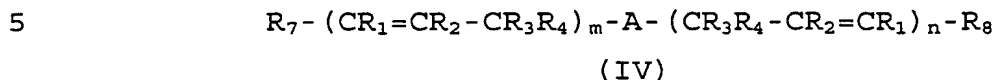
with p corresponding to the same definition as that
 20 given above.

Another particular polymer in accordance with the present invention may correspond to the following formula:



25 the radicals R_5 , which may be identical or different, corresponding to the same definition as that given above, and the p_1 , p_2 and p_3 , which may be identical or different, being integers ranging from 2 to 5000.

Further particular polymers in accordance with the present invention correspond to formula (IV) below:

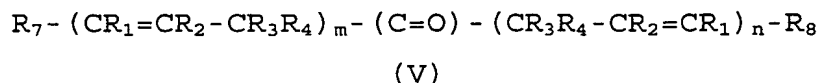


in which the radicals R_1 , R_2 , R_3 and R_4 are as defined above, A represents a C=O group, a CO derivative or -CHOH, and the radicals R_7 and R_8 , which may be identical or different, represent a linear or branched alkyl group containing from 1 to 20 carbon atoms, a cycloalkyl group containing from 3 to 20 carbon atoms or an aryl group containing from 6 to 20 carbon atoms, m is an integer ranging from 2 to 5000 and n is an integer ranging from 2 to 5000.

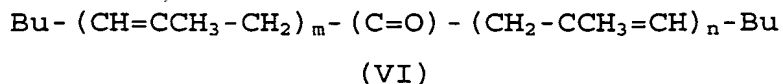
The term "C=O group" means, in the text hereinabove or hereinbelow, a group resulting from a nucleophilic addition of a nucleophilic reagent to -C=O, such as an imine, oxime or hydrazine group.

The polymers of formula (IV) are therefore linear polymers whose sequence of units (I) comprises a group A as defined above.

In formula (IV), the group A may represent -(C=O)-, in which case the corresponding polymer corresponds to formula (V) below:

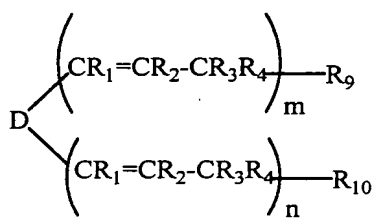


When R_1 , R_3 and R_4 represent H, R_2 represents a methyl group and R_7 and R_8 correspond to a linear butyl group (referred to as Bu in the above formula), the polymer corresponds to formula (VI) below:



with m and n corresponding to the same definition as that given above .

5 Finally, among the polymers in accordance with the present invention, examples that may be mentioned include the polymers corresponding to formula (VII) below:



(VII)

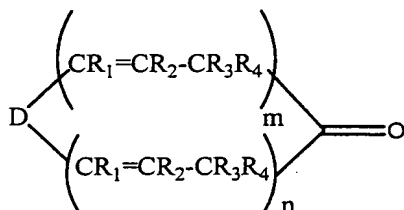
in which:

- the radicals R_1 , R_2 , R_3 and R_4 correspond to the same definition as that given above;
- the radicals R_9 and R_{10} , which may be identical or different, represent an OH, NH_2 , SH, optionally substituted amide or -CHO group, a group derived from -CHO, an ester group, an optionally substituted amide group or an azide group $-\text{N}_3$; or R_9 and R_{10} together form a $-\text{C}(=\text{O})-$ group, a group derived from CO or a -CHOH- group;
- D represents a linear or branched alkylenediyl group containing from 4 to 20 carbon atoms, possibly comprising in its chain one or more heteroatoms chosen from oxygen, sulfur and nitrogen,
- m is an integer ranging from 2 to 5000 and n is an integer ranging from 2 to 5000 .

The polymers of formula (VII) may correspond to linear polymers whose sequence of units

of formula (I) comprises a group D but may also correspond to cyclic polymers whose sequence of units comprises a group D and a $-C(=O)-$, $CHOH$ or $-C(NOH)-$ group.

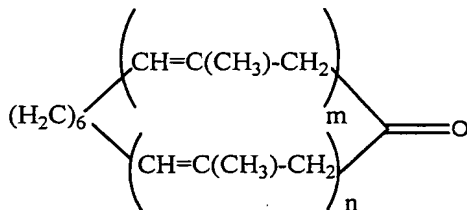
5 In formula (VII) above, the polymer may correspond, as stated previously, to a cyclic polymer, which is the case when the groups R_9 and R_{10} together form a $-(C=O)-$ group and D a linear or branched alkylenediyl group ranging from 4 to 20 carbon atoms,
 10 this polymer thus corresponding to formula (VIII) below:



(VIII)

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In the particular case where R_1 , R_3 and R_4 represent H, R_2 represents a methyl group and D an alkylene group $-(CH_2)_6-$, the polymer corresponds to formula (IX) below:

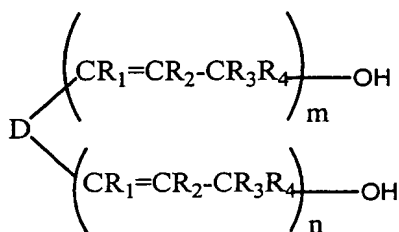


(IX)

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m and n corresponding to the same definition as that given above.

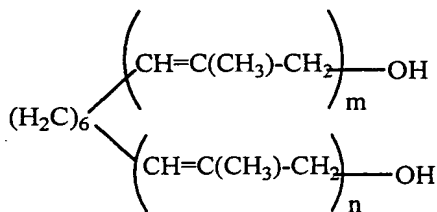
The groups R_9 and R_{10} may also both represent the same groups, in which case the polymer in question is a linear polymer with two identical ends. A particular example of this type of polymer is a polymer in which R_9 and R_{10} both represent, for example, groups -OH and D represents a linear or branched alkylene group, in which case the corresponding polymer is a linear polymer corresponding to formula (X) below:



10

(X)

When D corresponds to a linear alkylene group containing 6 carbon atoms, the polymer corresponds to formula (XI) below:



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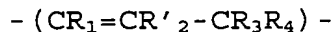
(XI)

According to the invention, the endo ethylenic unsaturation of the units in accordance with the present invention may predominantly have E geometry, the resulting polymer thus having E stereochemistry of the double bonds.

A subject of the present invention is also processes for preparing polymers comprising a sequence

of units, the said sequence containing an ethylenic unsaturation every 3 carbon atoms.

In general, a subject of the invention is a process for preparing a polymer whose skeleton
5 comprises a sequence of units of formula (I'):



(I')

the radicals R_1 , R_3 and R_4 corresponding to the same definition as that given above, R'_2 corresponding to
10 the same definition as R_2 and possibly also representing a hydrogen, the said process comprising a step consisting in reacting, in suitable amount:

- at least one compound of ylide type corresponding to formula (2) below:



in which the radicals R_1 , R'_2 , R_3 and R_4 correspond to the same definition as that given above, E being a leaving group,

- 20 - with a trivalent boron compound, comprising at least one group capable of migrating, so as to obtain the said sequence of units of formula (I') as defined above.

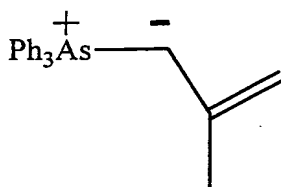
The term "trivalent boron compound" means a
25 boron-based group bearing three groups. The term "group capable of migrating" means a group capable of moving from the boron atom to an adjacent carbon atom by displacement of the bond, under the reaction conditions.

30 Preferably, the group capable of migrating formed by the boron compound may be chosen from linear

or branched alkyl groups containing from 1 to 20 carbon atoms, with the exception of branched alkyl groups linked to the boron via a tertiary carbon.

Preferably, the leaving group E may be
5 chosen from N_2 , $S(R)_2$, $S(O)(R)_2$, $N(R)_3$, $AsAr_3$ and PAR_3 , in which Ar represents a phenyl group optionally substituted with methyl or methoxy groups and R is an alkyl group, such as an alkyl group containing from 1 to 20 carbon atoms.

10 In particular, the compound of ylide type may be methallyltriphenylarsonium ylide of formula:



This ylide especially has the advantage of being easy to prepare.

15 Thus, the formation of the sequence of units of formula (I') according to the invention is based, surprisingly, on the following reaction characteristics:

- by virtue of the electron deficiency of the boron
20 atom, the boron compound is capable of receiving the negative charge borne by the carbon atom bearing the group R_1 , to form a complex;
- the complex thus obtained is unstable, due to the fact that the boron compound forming the complex
25 with the ylide compound bears an excess of negative charge and rearranges by 1,2 migration of one of the groups (or of the group, if there is only one) capable of migrating from the boron compound to the

carbon bearing R_1 , thus resulting in the concomitant loss of the leaving group E;

- the borane compound thus formed rearranges, surprisingly, according to a 1,3 sigmatropic rearrangement, whereas this compound would have been expected to react with another ylide compound. This rearrangement is characterized by the displacement of the boron-based group and, concomitantly, by a displacement of the double bond between the carbon atom bearing R_1 and the carbon atom bearing the migrating group initially borne by the boron-based compound;
- the borane compound resulting from the sigmatropic rearrangement may once again form a complex by addition to a new ylide molecule, followed by a new 1,2 migration and a 1-3 rearrangement, the reaction possibly continuing until the stock of ylide has been depleted. Sequences of units (I') characterized by the presence of an ethylenic unsaturation every 3 carbon atoms are thus obtained after these steps.

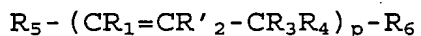
It is understood that the proportions of ylide and of initial boron compound may be readily determined by a person skilled in the art, as a function of the desired sequence length and of the size of the desired polymer.

It is noted that, starting with one equivalent of boron compound, the same amount of desired units may be obtained by adding to this equivalent of boron compound the same equivalent of ylide and of desired units.

More precise reaction mechanisms are proposed hereinbelow, concerning the process for preparing particular polymers in accordance with the invention.

5 In detail, the implementation of the process according to the invention begins with the formation of the ylide compound in an apolar aprotic solvent, such as anhydrous THF. The ylide compound is prepared by proceeding via a diazonium intermediate, to
10 which is added a base. The diazonium intermediate is prepared via usual methods available to those skilled in the art. The boron compound is then introduced and, finally, the compound of ylide type is added, preferably dropwise.

15 The invention relates in particular to a process for preparing a polymer of formula (II') below:

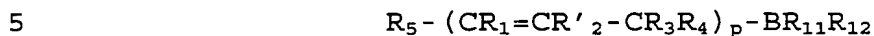


(II')

comprising a step of reacting, in suitable amount, a
20 boron compound of formula (1) $R_5 - BR_{11}R_{12}$ with R_5 having the same definition as that given above and representing the group capable of migrating, R_{11} and R_{12} , which may be identical or different, possibly:

- representing a branched alkyl group linked to the
25 boron via a tertiary carbon containing from 4 to 20 carbon atoms, an alkoxy group containing from 1 to 20 carbon atoms or an aryloxy group containing from 1 to 20 carbon atoms; or
- together forming a group $-O-X-O-$, in which X is a
30 linear or branched alkylenediyl group containing from 2 to 6 carbon atoms

with at least one allylic nucleophilic compound of the ylide type of formula (2) as defined above, by means of which an intermediate of formula (XII) below is obtained:

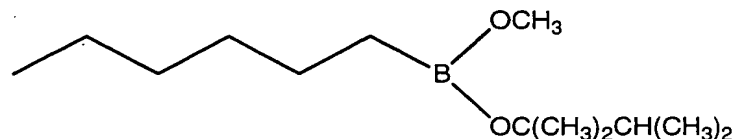
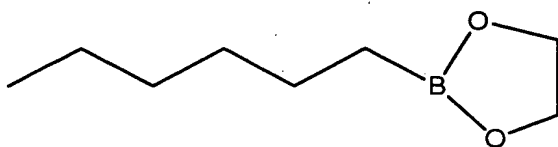


(XII)

the said process also comprising a step of converting the boron-based group into a suitable group R_6 , by means of which the polymer of formula (II') defined above is obtained.

It is noted that, for this process, the boron compound comprises only one group capable of migrating (group R_5), the groups R_{11} and R_{12} , by their nature, being incapable of migration.

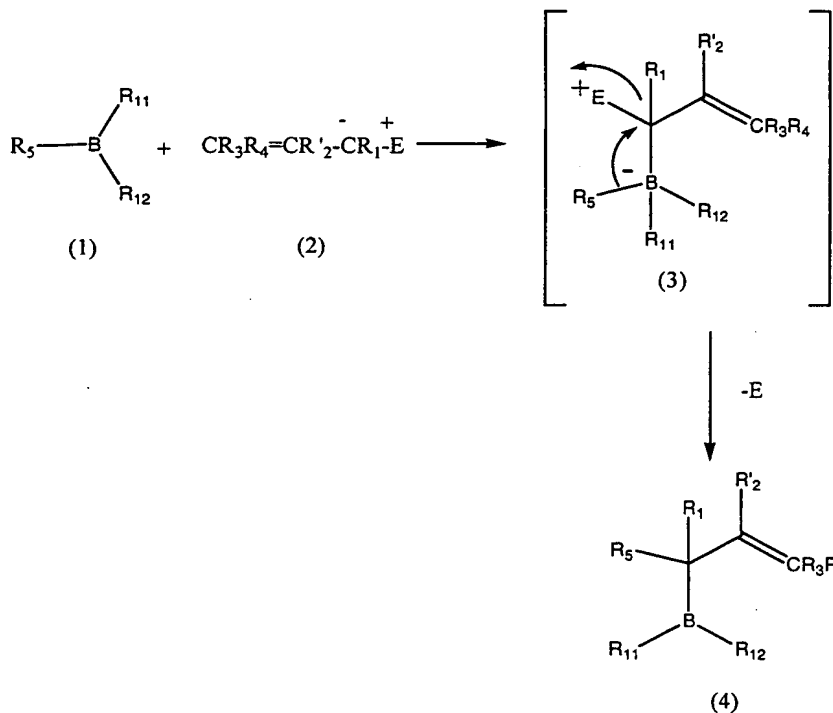
Examples of particular boron compounds that may be mentioned include the compounds having the following formulae:



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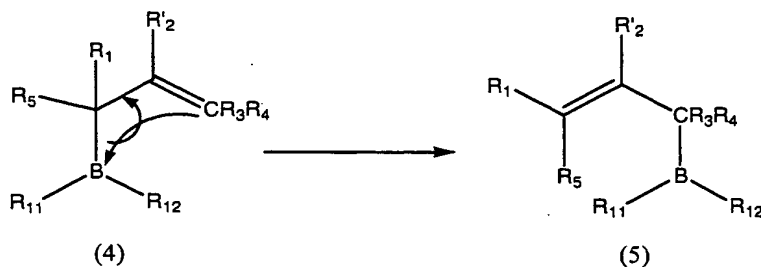
In order to make the description clearer, this implementation process will now be described by means of a reaction mechanism, comprising the following steps

- in the first step, the boron compound $R_5-BR_{11}R_{12}$ (1) reacts with the allylic nucleophilic compound (2), leading to a complex (3), which spontaneously rearranges via a migration of 1,2 type of the group R_5 , to give an intermediate compound (4):



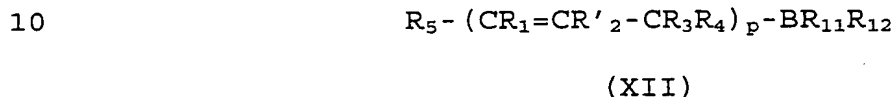
The intermediate compound (4) differs from the initial boron compound (1) by the fact that a unit $(CR_3R_4=CR'_2)-CR_1$ has become inserted into the boron-carbon bond $B-R_5$.

- in a second stage, the intermediate compound (4) rearranges again via a 1,3-sigmatropic rearrangement mechanism according to the following scheme:



This second rearrangement is faster than the intermediate reaction (4) with the allylic nucleophilic compound of ylide type (2).

5 The borane compound (5) obtained during this second step can participate in a new polymerization step to give, after reaction with several equivalents of ylides, the polymer having the following formula:



Finally, the last step consists in
15 converting, by reaction with a suitable reagent, the
group $BR_{11}R_{12}$ into a suitable group R_6 .

By way of examples, for converting the group $-BR_{11}R_{12}$ into an $-OH$ group, the polymer of formula (XII) may be subjected to an oxidizing solution of hydrogen peroxide H_2O_2 in basic medium (for example 3M NaOH). Other oxidizing agents commonly used are m-chloroperbenzoic acid and triethylamine oxide.

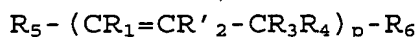
To convert the group $-BR_{11}R_{12}$ into an $-NH_2$ group, the polymer of formula (XII) may be subjected to a solution of hydroxylamine-O-sulfonic acid NH_2-O-SO_3H or of chloramine NH_2Cl in basic medium.

Finally, to convert the group $\text{-BR}_{11}\text{R}_{12}$ into a -CHO group, given that the radicals R_{11} and R_{12}

represent alkoxy groups, the polymer of formula (XII) may be subjected to an organolithium reagent, for example methoxymethyl thiophenyl ether, followed by a treatment with mercuric chloride (HgCl_2) and a treatment with aqueous hydrogen peroxide solution in basic medium.

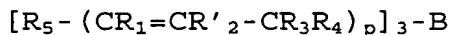
Via this process, polymers with an end R_5 derived from the starting boron compound and an end R_6 resulting from the chemical conversion of the group $\text{BR}_{11}\text{R}_{12}$.

According to one variant of the invention, the process for preparing a polymer of formula (II) below:



(II')

comprises a step of reacting, in suitable amount, a boron compound of formula $(\text{R}_5)_3\text{-B}$ with R_5 having the same definition as that given above, with at least one allylic nucleophilic compound of the ylide type of formula (2) as defined above, by means of which an intermediate of formula (XIII) below is obtained:



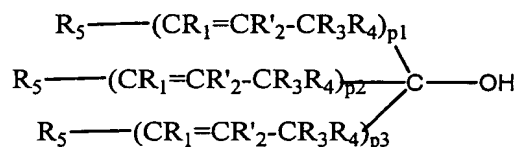
(XIII)

the said process also comprising a step of converting the boron-based group into a suitable group R_6 , by means of which the polymer of formula (II') defined above is obtained.

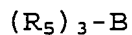
The reactions for conversion of the intermediate compound (XIII) into the polymer (II) are similar to those described for the conversion of the intermediate compound (XII).

In particular, a boron compound that may be used is the compound Bu_3B (Bu corresponding to the linear butyl group), and a nucleophilic compound of ylide type that may be used is methallyltriphenylarsonium ylide for which E corresponds to a Ph_3As group, by means of which the polymer of formula (III) defined above is obtained, after a final step of conversion, by treatment with aqueous hydrogen peroxide solution in basic medium.

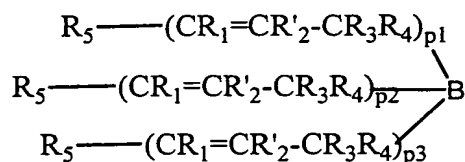
A process for preparing according to the invention a particular polymer corresponding to the following formula:



the radicals R_5 , which may be identical or different, corresponding to the same definition as that given above, and p_1 , p_2 and p_3 , which may be identical or different, being integers ranging from 2 to 5000, comprises a step of reacting, in suitable amount, a boron compound of formula:



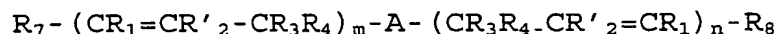
with at least one allylic nucleophilic compound of the ylide type of formula (2) as defined above, by means of which an intermediate of formula (XIV) below is obtained:



(XIV)

the said process also comprising a step of converting the boron-based group into a C-OH group by treatment of the intermediate compound (XIV) by heating in the presence of carbon monoxide, preferably at 150°C in the presence of ethylene glycol, followed by a treatment with aqueous hydrogen peroxide solution in basic medium.

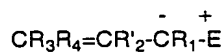
The invention also relates to a process for preparing a particular polymer in accordance with the invention, the said polymer corresponding to formula (IV') below:



(IV')

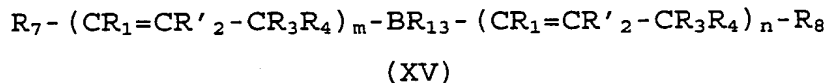
with R_1 , R'_2 , R_3 , R_4 , R_7 , R_8 , A , m and n having the same definition as that given above, the said process comprising the reaction:

- of a boron compound of formula (6) $R_7 - BR_8 R_{13}$ with R_7 and R_8 having the same definition as that given above, R_{13} being a branched alkyl group linked to the boron via a tertiary carbon containing from 4 to 20 carbon atoms, or an alkoxy or aryloxy group containing from 1 to 20 carbon atoms;
- with at least one allylic nucleophilic compound of the ylide type of formula (2):



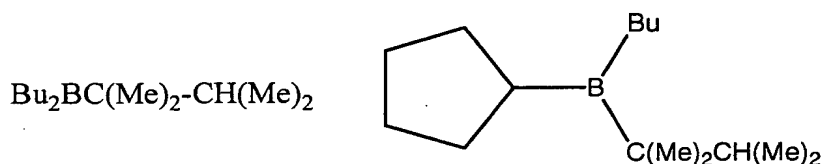
(2)

as defined above, in order to obtain a derivative of formula (XV):



- 5 followed by a reaction for conversion of the group BR_{13} into a suitable group A.

Examples of boron compounds that may be mentioned include the particular compounds corresponding to the following formulae:



10

Bu corresponding to the linear butyl group.

For example, to go from the function BR_{13} to CO, the following treatments may be applied:

- 15 - treatment with carbon monoxide, in the presence of water, at a pressure, for example, of 100 bar and a temperature of at least 70°C;

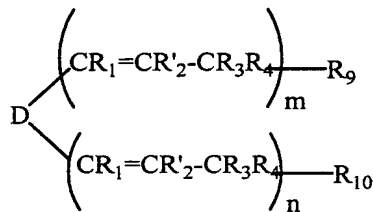
- treatment with NaCN in the presence of $(CF_3CO)_2O$, followed by a treatment with aqueous hydrogen peroxide solution in basic medium;

- 20 - if R_{13} represents an alkoxy group, treatment with dichloromethyl methyl ether, in the presence of lithium triethylmethyllate, followed by a treatment in the presence of aqueous hydrogen peroxide solution in basic medium.

- 25 Once the CO function has been obtained, it is clear that derived functions (oxime, imine, alcohols) may be accessed via standard treatments within the scope of a person skilled in the art. For

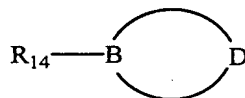
example, to go from the CO function to the C=NOH function, a treatment with hydroxylamine may be envisaged, whereas, in order to obtain a CHOH function, the CO function may be reduced using a reagent such as sodium borohydride.

Finally, a subject of the present invention is a process for preparing a particular polymer of formula (VII') below:



(VII')

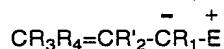
as defined above, the said process comprising a step of reacting a cyclic boron compound of formula (7):



(7)

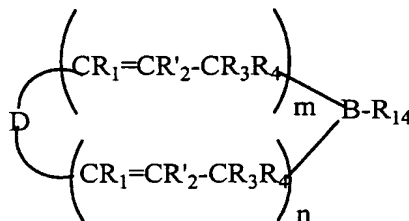
R₁₄ representing a group chosen from branched alkyl groups linked to the boron via a tertiary carbon containing from 4 to 20 carbon atoms, alkoxy groups containing from 1 to 20 carbon atoms or aryloxy groups containing from 6 to 20 carbon atoms, D having the same definition as that given above

with at least one nucleophilic compound of ylide type of formula (2):



(2)

as defined above, in order to obtain a derivative of formula (XVI):



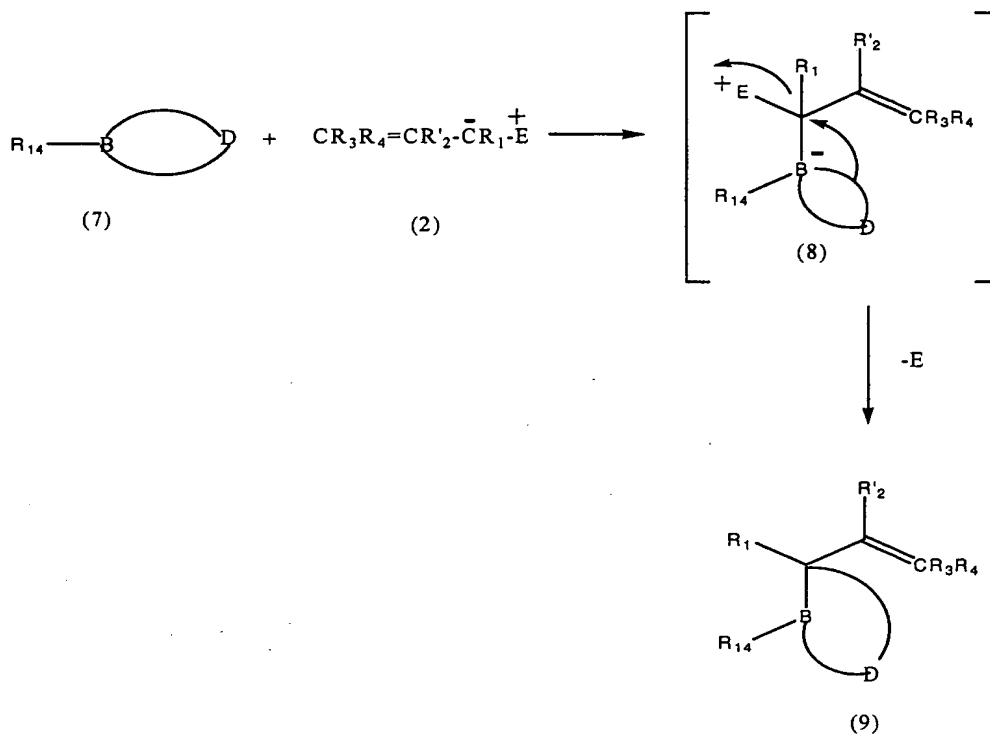
(XVI)

- 5 followed by a step of converting the group BR_{14} into suitable groups R_9 and R_{10} .

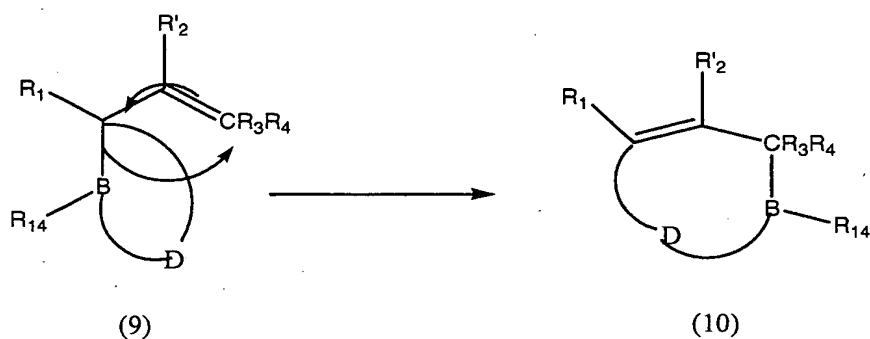
Thus, this process corresponds to the preparation of a polymer in accordance with the present
 10 invention from a cyclic boron compound. During this process, expansion of the boron-based ring takes place, via 1,2 migration of the C-B bonds of the ring, whereas R_{14} is incapable of undergoing this migration.

In order to make the description clearer,
 15 this process will now be described by means of the following reaction mechanism:

- in a first stage, the cyclic boron compound (7) reacts with the allylic nucleophilic compound (2), leading to a complex (8), which spontaneously
 20 rearranges, via 1,2 migration of a carbon-boron bond of the cyclic compound, to give compound (9) according to the following scheme:

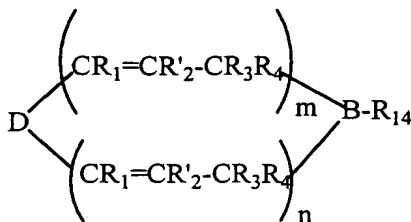


5 - in a second stage, compound (9) rearranges via a mechanism of 1,3-sigmatropic rearrangement according to the following scheme:



10 Compound (10) obtained during this second step can participate in a new polymerization step to

give, after reaction with several equivalents of ylides, the polymer of formula (XIV) below:



(XVI)

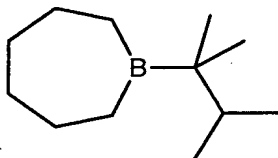
5

Next, a final step consists in converting the group $B-R_{14}$ into suitable groups $-R_9$ and R_{10} .

The reactions that may be envisaged for conversion of the group R_{14} are similar to those envisaged for conversion of the group $BR_{11}R_{12}$ into a group R_6 .

An example that may be mentioned, as a cyclic boron compound in accordance with the definition of compound (7), is the B-thexylborepane of formula:

15



for which the thexyl group $-C(CH_3)_2-CH(CH_3)_2$ is incapable of migrating according to a 1,2 migration ("non-labile" group), and as such the unit $-(CR_1=CR_2-CR_3R_4)-$ will become inserted into the ring to give a cyclic intermediate.

When the process includes B-thexylborepane as boron compound and, as allylic nucleophilic compound of ylide type, the methallyltriphenylarsonium ylide for

25

which E corresponds to the Ph_3As group, and when this reaction is followed by a step of conversion via the action of aqueous hydrogen peroxide solution in basic medium, the polymer of formula (XI) defined above is
5 obtained. When the step of conversion consists of a carbonylation step, the polymer obtained is the polymer of formula (IX) defined above. This step of conversion to a ketone consists, for example, in treating the boron-based polymer (XVI) with sodium cyanide followed
10 by trifluoroacetic anhydride and then with aqueous hydrogen peroxide solution in basic medium.

The polymers according to the invention are particularly advantageous, since they may find an application in numerous sectors.

15 Thus, they may be used for the manufacture of fibres, resins or films, the manufacture of articles requiring relatively rigid materials, for example for the manufacture of plugging seals, sheaths or coatings for insulating conductive materials.

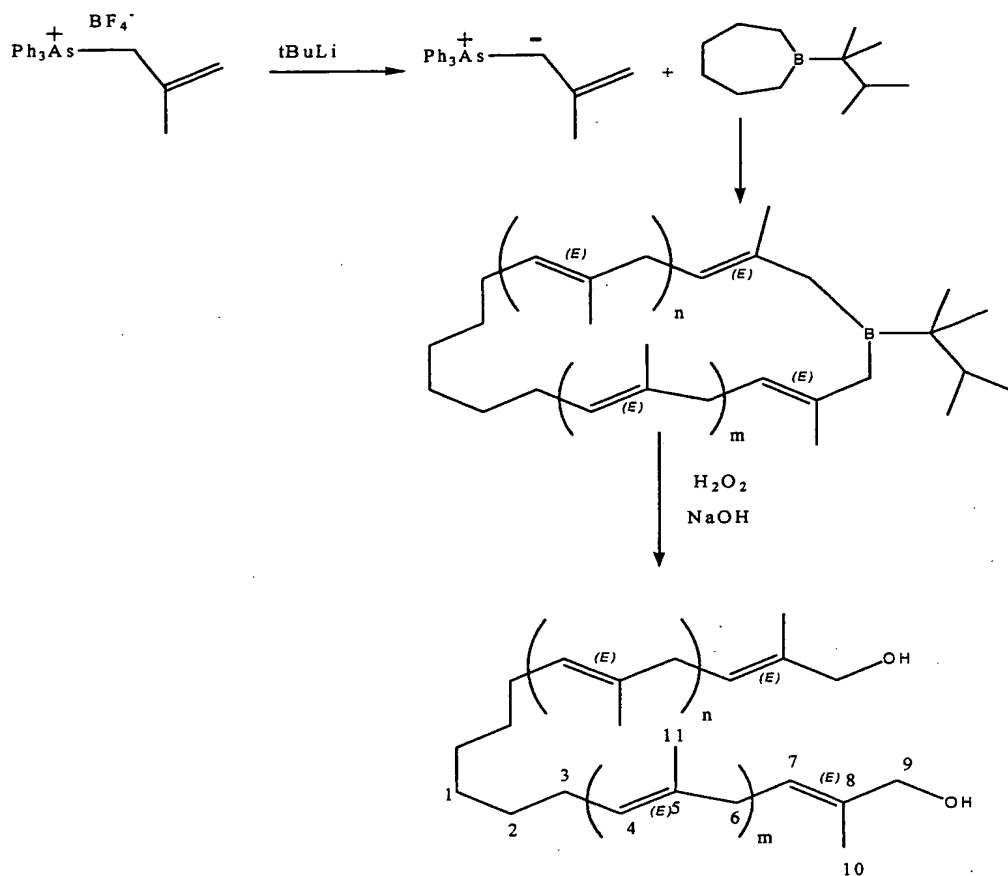
20 The polymers comprising polar functions may be used, for example, for making glues or adhesives.

The invention will now be described relative to the examples that follow, which are given as non-limiting illustrations.

25 **EXAMPLE 1.**

Example 1 presents an example of preparation of a linear polymer included in the context of the definition of the polymers of formula (VII) with R_1 , R_3 and R_4 representing H, R_2 represents $-\text{CH}_3$, R_9 and
30 R_{10} represent $-\text{OH}$ and D represents $-(\text{CH}_2)_6-$.

The reaction scheme is as follows:



The protocol for preparing this type of polymer is as follows:

1.33 mL (2 mmol, 10 eq.) of a tert-butyl lithium solution (1.5 M in pentane) are added dropwise to a suspension of 0.896 g (2 mmol, 10 eq.) of methallyltriphenylarsonium tetrafluoroborate in 15 mL of anhydrous THF under an argon atmosphere, cooled to -78°C . The solution immediately turns orange and becomes clear. Stirring is continued at this temperature for 30 minutes and the mixture is then placed in an ice bath. The temperature is allowed to stabilize (15 minutes) and a solution of 38.4 mg (0.2 mmol, 1 eq.) of cyclic borane in 1 mL of anhydrous THF is then added. The solution decolourizes over 1 hour.

3 mL of 30% hydrogen peroxide and 3 mL of 3N sodium hydroxide are then added. The mixture returns to room temperature and stirring is continued for 4 hours, 30 mL of saturated ammonium chloride solution are then
5 added and the mixture is extracted with 3 times 70 mL of dichloromethane. The organic phase is dried over magnesium sulfate and then filtered and evaporated. A white solid is obtained. This crude mixture is adsorbed onto silica and then placed on a column of silica gel
10 and eluted with a 2/5/3 hexane/ether/dichloromethane mixture to give a colourless oil. A white solid forms after addition of 50 mL of methanol. The suspension is filtered and the solid is washed with twice 20 mL of methanol and then dried under vacuum. The polymer is
15 recovered in the form of a white solid (112 mg, yield = 81%).

^1H NMR (CDCl_3 , δ in ppm): 5.17-5.12 (br t, 283 H, H4), 4.01 (s, 2H, H9), 2.69-2.67 (br d, 604H, H6), 1.66-1.58
20 (br s, 921H, H10-H11).

^{13}C NMR (CDCl_3 , δ in ppm): 136.11-135.34 (br s, C5), 122.40-121.88 (br s, C4), 38.58-32.03 (br s, C6), 16.48-16.22 (br s, C11).

25

The polymer obtained is also analysed by stearic exclusion chromatography.

The analysis conditions are as follows:

type of column: PL gel 100+1000

30 Eluent: THF

pump flow rate: 1.00 mL/minute

The sample to be analysed has a concentration of 1.45 mg/mL, with a refractive index increment dn/dc set at 0.130 mL/g.

The results of the measurements by LALLS (little-angle laser light scattering) are as follows:

Degree of polymerization	$D_p=424= n+m$
Number-average molar mass	$M_n=23040 \text{ g/mol}$
Weight-average molar mass	$M_w=33750 \text{ g/mol}$
Polydispersity index	$DPI= M_w/M_n=1.46$

10

Under the same operating conditions as those mentioned above, 0.896 g (2 mmol, 50 eq.) of arsonium salt react with 7.7 mg (0.04 mmol, 1 eq.) of cyclic borane to give after oxidation a polymer of the same structure (83 mg, yield = 74%).

The polymer obtained is also analysed by stearic exclusion chromatography.

The analysis conditions are as follows:

Type of column: PL gel 100+1000

20 Eluent: THF

Pump flow rate: 1.00 mL/minutes

The sample to be analysed has a concentration of 1.66 mg/mL, with a dn/dc set at 0.130 mL/g.

The results of the LALLS measurements are as follows:

$DP=490$

$M_n=26470 \text{ g/mol}$

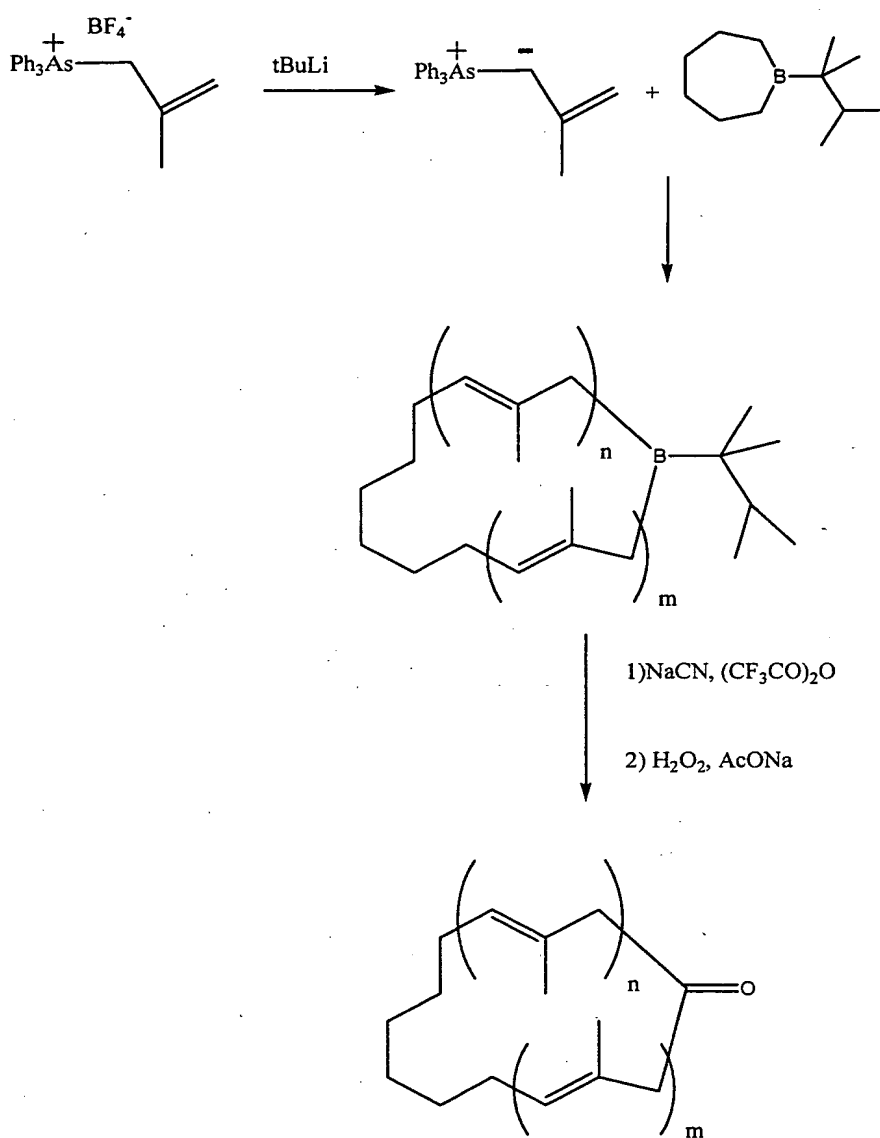
$M_w=39600 \text{ g/mol}$

30 $DPI= M_w/M_n=1.50.$

EXAMPLE 2.

Example 2 presents the case of a cyclic polymer falling within the context of the family of polymers of formula (VII), with R_9 and R_{10} together forming a $-(C=O)-$ group, D an alkylene $-(CH_2)_6-$, R_1 , R_3 and R_4 represent H, and R_2 represents $-CH_3$.

The reaction scheme is as follows:



1.33 mL (2 mmol, 10 eq.) of tert-butyl lithium (1.5M in pentane) are added dropwise to a suspension of 0.896 g (2 mmol, 10 eq.) of methallyltriphenylarsonium tetrafluoroborate in 15 mL of anhydrous THF under an argon atmosphere, cooled to -78°C. The solution immediately turns orange and becomes clear. Stirring is continued at this temperature for 30 minutes and the mixture is then placed in an ice bath. The temperature stabilizes at 0°C (15 minutes) and a solution of 38.4 mg (0.2 mmol, 1 eq.) of cyclic borane in 1 mL of anhydrous THF is then added. The solution decolourizes over 1 hour. The mixture is then placed at room temperature, and 20 mg (0.4 mmol, 2 eq.) of NaCN are then added. The mixture is then stirred vigorously at room temperature for 2 hours. The solution turns slightly yellow. The temperature is then reduced to -78°C and 62 µL (0.44 mmol, 2.2 eq.) of trifluoroacetic anhydride are added. A precipitate appears. The temperature is maintained at -78°C for 10 minutes and the mixture is then placed at room temperature. Stirring is continued for 5 hours, and 3 mL of 30% hydrogen peroxide and 3 mL of a 3N sodium acetate solution are then added. The mixture is stirred for 5 hours and is then extracted with 3 times 50 mL of dichloromethane. The organic phases are combined and washed with 20 mL of 1N hydrochloric acid. The solution is dried over magnesium sulfate and filtered, and the solvents are evaporated off. The crude product is adsorbed onto silica, placed on a column of silica gel and then eluted with a 3/6/1 hexane/ether/dichloromethane mixture. A colourless oil

is thus recovered, which converts into a white solid after addition of 20 mL of methanol. The polymer is then washed with twice 10 mL of methanol and is isolated in the form of a white solid (56 mg, 43%).

5 Molar mass of the (2-methyl)prop-1-enylidene unit: 54 g/mol.

Molar mass of the cyclohexanone unit: 112 g/mol

Molar mass of the polymer: $(112 + (n+m)54)$ g/mol

10 The polymer obtained is also analysed by stearic exclusion chromatography.

The analysis conditions are as follows:

Type of column: PL gel 100+1000

Eluent: THF

15 Pump flow rate: 1.00 mL/minute

The sample to be analysed has a concentration of 1.82 mg/mL, with dn/dc set at 0.130 mL/g.

The results of the LALLS measurements are
20 as follows:

$D_p=481$

$M_n=26050$ g/mol

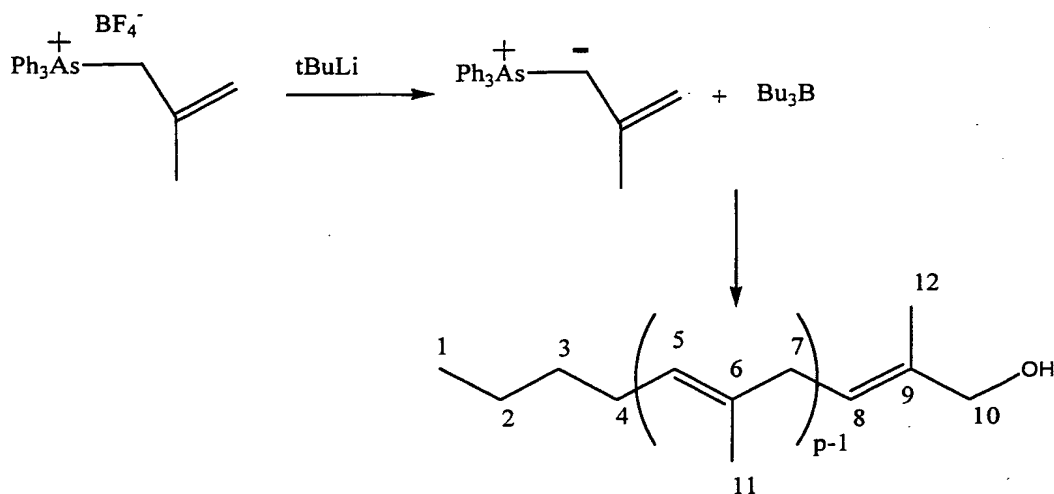
$M_w=35730$ g/mol

$DPI= M_w/M_n=1.37$.

25 **EXAMPLE 3.**

Example 3 presents an example of preparation of a linear polymer included in the context of the definition of the polymers of formula (II) with R_1 , R_3 and R_4 representing H, R_2 representing $-CH_3$, R_5
30 representing $CH_3-(CH_2)_3-$ (denoted as Bu), and R_6 representing $-OH$.

The reaction scheme is as follows:



5

1.2 mL (1.8 mmol, 9 eq.) of a solution of tert-butyl lithium (1.5M in pentane) are added dropwise to a suspension of 0.806 g (1.8 mmol, 9 eq.) of methallyltriphenylarsonium tetrafluoroborate in 15 mL of anhydrous THF, under an argon atmosphere, cooled to -78°C. The solution turns bright orange and clear. Stirring is continued for 30 minutes at -78°C and then for 15 minutes at 0°C. A solution containing 0.2 mL (0.2 mmol, 1 eq.) of tributylborane (1M in THF) in 2 mL of anhydrous THF is cooled in an ice bath, and then added dropwise. Total decoloration takes place 10 minutes after the end of the addition. 3 mL of 30% hydrogen peroxide and then 2 mL of 3N sodium hydroxide are added. The mixture is stirred for 4 hours at room temperature. 30 mL of saturated ammonium chloride solution are added and the reaction medium is then extracted with 3 times 50 mL of dichloromethane. The organic phase is dried over magnesium sulfate and then

filtered and evaporated. The crude mixture is adsorbed onto silica and the product is placed on a column of silica gel and then eluted with an 8/2 hexane/ether mixture. The polymer is obtained in the form of a
5 colourless oil (125 mg, yield = 89%).

Molar mass of the (2-methyl)prop-1-enylidene unit:
54 g/mol.

Molar mass of the hexanol unit: 74 g/mol

10 Molar mass of the polymer: $(74 + p54)$ g/mol.

The average degree of polymerization determined by NMR is $DP=p+1=12$.

15 ^1H NMR (CDCl_3 , δ in ppm): 5.45-5.40 (br t, 1H, H8),
5.17-5.12 (t app, 11.2 H, H5), 4.13 (s, 0.3 H, H10),
4.02 (s, 1.7H, H10'), 2.74-2.64 (m, 25H, H7), 2.00-1.96
(m, 2H, H4), 1.68-1.66 (m, 3H, H12), 1.60-1.56 (m, 33.9
H, H11) 1.33-1.21 (m, 4.6H, H2-H3), 0.90-0.81 (m, 3H,
20 H1).

^{13}C NMR (CDCl_3 , δ in ppm): 135.91-135.26 (m), 135.14,
135.43, 124.69, 124.34, 123.08-122.43 (m), 69.08,
38.35-37.66 (m), 31.27, 30.75, 30.46, 29.84, 27.77,
23.60, 16.25, 13.77.

25

Under the same operating conditions, starting with 896 mg (2 mmol, 20 eq.) of the same arsonium salt and 0.1 mL (0.1 mmol, 1 eq.) of tributylborane, and after oxidation, a polymer of the
30 same structure is obtained (93 mg, 81 %).

^1H NMR (CDCl_3 , δ in ppm): 5.42 (m, 1H, H8), 5.1-5.12 (t
app, 25.3 H, H5), 4.13 (s, 0.2 H, H10), 4.01 (s, 1.8H,
H10'), 2.74-2.64 (m, 58H, H7), 1.99-1.94 (m, 2H, H4),
1.68-1.66 (m, 5H, H12), 1.60-1.56 (m, 91 H, H11) 1.33-
5 1.21 (m, 4.6H, H2-H3), 0.90-0.81 (m, 3H, H1).

The average degree of polymerization
determined by NMR is $\text{DP}=26$.